

DESCRIPTION

GREASE COMPOSITION FOR AUXILIARY MACHINERY OF AUTOMOBILE
ELECTRICAL COMPONENT AND ROLLING BEARING HAVING THE GREASE
COMPOSITION PACKED THEREIN

<TECHNICAL FIELD>

The present invention relates to a grease composition which is used especially under severe conditions of high temperature, high speed, high load and vibration in automobile electrical parts or auxiliary machineries of engines such as alternators, intermediate pulleys, and electromagnetic clutches for car air conditioners and further which is used for parts required to have fluidity at an extremely low temperature of -40°C, and to a rolling bearing having the foregoing grease composition packed therein.

<BACKGROUND ART>

In automobiles, by the spread of FF (front engine front drive) vehicles aiming at miniaturization and lightening and the demands of enlargement of an accommodation space, a reduction of the engine room space is unavoidable, miniaturization and lightening of the above-enumerated electrical parts and auxiliary machineries of engines are further being advanced, and

respective parts to be integrated thereinto are required to have high performance and realize a high output more and more. However, a lowering of the output due to the miniaturization is inevitable. For example, in alternators and electromagnetic clutches for car air conditioners, the lowering of the output is compensated by accelerating the speed, and following this, intermediate pulleys are actuated at a high speed. Further, by the demand for improving silence properties, since closing of an engine room is advancing and an increase of the temperature within the engine room is promoted, it has become necessary that these parts endure high temperatures.

For the sake of improving the seizure life at a high temperature, there have hitherto been made various proposals. For example, as described in JP-B-7-45677 and Japanese Patent Nos. 3,290,010 and 3,330,755, greases made of a trimellitic ester oil-containing base oil having a urea compound as a thickener blended therein are widely used. Also, in rolling bearings to be used for these applications, there is also required a countermeasure against a flaking phenomenon accompanied with a structural change of the transfer surface. For example, JP-A-2002-195277 and JP-A-2003-13973 propose a method for adding a metal passive agent such as nitrous acid.

Automobiles are used in various countries and states of the world, the use environment thereof is diverse, and

required characteristics are diverse corresponding thereto. For example, in the cold district, a requirement for the non-generation of abnormal noises caused due to a shortage of fluidity of a lubricant at the time of start-up of engine is high; and in the tropical rain forest district and the district closed to the sea, since the humidity and salinity in the air are high, a requirement for rust preventing properties is high.

However, greases which can fully meet these diverse requirements inclusive of the above-enumerated greases have not been obtained yet. Then, an object of the invention is to provide a grease composition and a rolling bearing which do not generate abnormal noises even at an extremely low temperature of -40°C, have excellent seizure resistance even under a high temperature closed to 180°C, have excellent flaking resistance and rust preventing performance, and are suitable especially for the foregoing electrical parts and auxiliary machineries of engines, etc.

<DISCLOSURE OF THE INVENTION>

In order to solve the foregoing problems, the present inventors made extensive and intensive investigations. As a result, it has been found that among diurea compounds, those having an alicyclic hydrocarbon group, when combined with a base oil containing an aromatic ester oil, exhibit an excellent lubricating performance over a wide

temperature range of from an extremely low temperature to a high temperature, do not generate abnormal noises at a low temperature, and can improve greatly a seizure performance of a bearing, leading to accomplishment of the invention.

Specifically, the invention provides a grease composition for auxiliary machinery of automobile electrical component, which is characterized by containing a base oil containing an aromatic ester oil in an amount of 30 % by mass or more based on the whole amount of the base oil and a diurea compound, as a thickener, represented by the following general formula in an amount of from 5 to 35 % by mass based on the whole amount of the grease composition.

R8-NHCONH-R9-NHCONH-R10

(In the formula, R9 represents an aromatic hydrocarbon group having from 6 to 15 carbon atoms; and R8 and R10, which may be the same or different, each represents an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, or a fused ring).

Also, the invention provides the foregoing grease composition for auxiliary machinery of automobile electrical component, which is characterized by containing at least one member of carbon black and carbon nano tube

as a conductive powder for the purpose of imparting conductivity. Further, it is preferable that two or more members selected from rust preventives made of a carboxylic acid or a carboxylate, ester based rust preventives, and amine based rust preventives are contained as a rust preventive in an amount of from 0.2 to 10 % by mass in total and from 0.1 to 9.9 % by mass singly based on the whole amount of the grease composition, whereby sufficient rust preventing properties are imparted. Also, such rust preventives are free from adverse influences against the environment.

Also, the invention provides a rolling bearing, which is characterized by casing freely rollingly plural rolling elements by a cage between an inner race and an outer race and packing the foregoing grease composition for auxiliary machinery of automobile electrical component therein.

<BRIEF DESCRIPTION OF THE DRAWINGS>

Fig. 1 is a cross-sectional view to show a double row angular ball bearing as one embodiment of the rolling bearing of the invention; Fig. 2 is a graph to show the results of Verification-I of the content of an aromatic ester oil; Fig. 3 is a graph to show the results of Verification-I of the blending amount of a thickener; Fig. 4 is a graph to show Relationship-I between a pour point of a base oil and the generation of abnormal noises at a

low temperature; Fig. 5 is a graph to show the results of Verification-II of the content of an aromatic ester oil; Fig. 6 is a graph to show the results of Verification-II of the blending amount of a thickener; Fig. 7 is a graph to show Relationship-II between a pour point of a base oil and the generation of abnormal noises at a low temperature; Fig. 8 is a graph to show the relationship between the addition amount of carbon black and the generation probability of flaking; and Fig. 9 is a graph to show the relationship between the particle size of carbon black and the anderon value.

Also, in the drawings, symbol 10 stands for a double row angular ball bearing; 15 stands for an outer race; 16 stands for an inner race; 17 stands for an outer raceway; 18 stands for an inner raceway; and 19 stands for a rolling element (ball).

<BEST MODE FOR CARRYING OUT THE INVENTION>

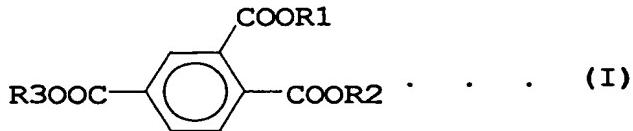
The grease composition for auxiliary machinery of automobile electrical component (hereinafter simply referred to as "grease composition") and the rolling bearing of the invention will be hereunder described in detail.

(Grease composition)

[Base oil]

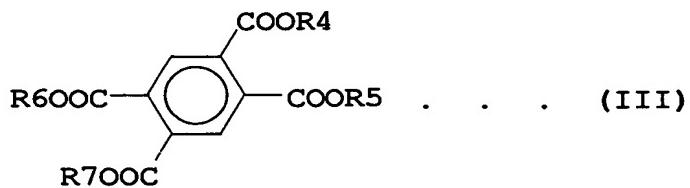
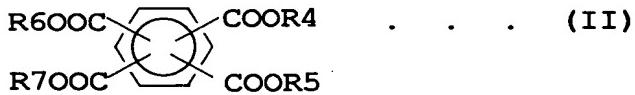
In the grease composition of the invention, the base

oil contains an aromatic ester oil. Of aromatic ester oils, trimellitic ester oils represented by the following formula (I) are preferable.



In the formula (I), R1, R2, and R3, which may be the same or different, each represents a saturated or unsaturated linear or branched hydrocarbon group. Also, those having from 6 to 10 carbon atoms are preferable.

Also, as the aromatic ester oil, pyromellitic ester oils represented by the following formulae (II) and (III) are preferable.



In the formula (II) and formula (III), R4, R5, R6, and R7, which may be the same or different, each represents a saturated or unsaturated linear or branched hydrocarbon group. Also, those having from 6 to 10 carbon atoms are preferable.

There have hitherto been known polyphenyl ether oils, silicone oils, fluorocarbon oils, and the like as a lubricant having excellent heat resistance. However, all of these lubricants are very expensive and involve such a problem that silicone oils and fluorocarbon oils are generally inferior in lubricity. In contrast, the foregoing aromatic ester oils are relatively cheap and have such an advantage that they are excellent in heat resistance, oxidation resistance, abrasion resistance, and the like. In particular, since the trimellitic ester oils and pyromellitic ester oils represented by the formulae (I) to (III) and containing a hydrocarbon group having from 6 to 10 carbon atoms have a low pour point and a high viscosity index, they are suitable for auxiliary machineries of automobile electrical components which are required to have a wide use temperature of from an extremely low temperature to a high temperature. Especially, the trimellitic ester oils have a low pour point and are preferable.

Such trimellitic ester oils and pyromellitic ester oils containing a hydrocarbon group having from 6 to 10 carbon atoms are available in the market; examples of the trimellitic ester oils include "TRIMEX T-08" and "TRIMEX N-08", all of which are manufactured by Kao Corporation, "ADEKA PROVER T-45", "ADEKA PROVER T-90" and "ADEKA PROVER PT-50", all of which are manufactured by Asahi Denka Co.,

Ltd., and "EMKARATE 8130" and "EMKARATE 9130", all of which are manufactured by UNIQEMA; and examples of the pyromellitic ester oils include "ADEKA PROVER LX-1891" and "ADEKA PROVER LX-1892", all of which are manufactured by Asahi Denka Co., Ltd.

The content of the foregoing aromatic ester oil is preferably 30 % by mass or more based on the whole amount of the base oil. When the content of the aromatic ester oil is less than 30 % by mass, seizure is likely caused at a high temperature, and the abrasion resistance is not thoroughly revealed. Examples of a lubricant which can be used jointly include mineral oils, fluorocarbon oils, silicone oils, synthetic hydrocarbon oils, ether oils, ester oils other than aromatic ester oils, and glycol oils. Of these, those which have a low pour point and which are excellent in heat resistance, oxidation resistance, etc. are preferable, and synthetic hydrocarbon oils, ether oils, and ester oils are suitable. Specifically, examples of the synthetic hydrocarbon oils include poly- α -olefin oils; examples of the ether based oils include alkyl diphenyl ethers and alkyl triphenyl ethers; and examples of the ester oils include diester oils, neopentyl type polyol ester oils, and complex ester oils thereof. They may be used singly or can be properly combined and used. Above all, taking into consideration not only low pitch sound fluidity while taking into account the generation of

abnormal noises at an extremely low temperature but also improvements in the lubricating performance and seizure life under severe conditions of high temperature, high speed, high load and vibration, a combined use with a polyol ester oil such as pentaerythritol ester oils, a poly- α -olefin oil, or an alkyl diphenyl ether oil is preferable.

Also, a kinematic viscosity at 40°C of the base oil is preferably from 30 to 150 mm²/s, and taking into consideration of the low-temperature fluidity, it is more preferably from 40 to 130 mm²/s. It is most preferably from 40 to 100 mm²/s.

[Thickener]

The foregoing base oil is blended with a diurea compound represented by the following formula (IV) as a thickener.



In the formula (IV), R₉ represents an aromatic hydrocarbon group having from 6 to 15 carbon atoms; and R₈ and R₁₀, which may be the same or different, each represents a hydrocarbon group or a fused ring hydrocarbon group. Also, in R₈ and R₁₀, the hydrocarbon group may be any of an aliphatic hydrocarbon group or an aromatic hydrocarbon group; and the fused ring hydrocarbon group

preferably has from 9 to 19 carbon atoms. It is preferable that R8 and R10 each contains at least an alicyclic hydrocarbon group or an aliphatic hydrocarbon group. A diurea compound containing an alicyclic hydrocarbon group has such properties that it has excellent heat resistance as compared with a diurea compound containing an aliphatic hydrocarbon group. The diurea compound containing an aliphatic hydrocarbon group has such an advantage that when used as a thickener of grease, it is excellent in fluidity of the grease as compared with the diurea compound containing an alicyclic hydrocarbon group. Also, the diurea compound containing an alicyclic hydrocarbon group or an aliphatic hydrocarbon group has a large surface area per unit volume and a high thickening effect as compared with a diurea compound containing an aromatic hydrocarbon group due to a difference of the fibrous shape thereof. For that reason, when compared in terms of the same penetration, the diurea compound containing an aliphatic hydrocarbon group or an alicyclic hydrocarbon group may be made small in the use amount as compared with the diurea compound containing an aromatic hydrocarbon group so that the proportion of the base oil can be increased in proportion thereto and that the seizure resistance can be improved.

The diurea compound represented by the foregoing formula (IV) is obtained by reacting 2 moles in total of a

monoamine containing R8 or R10 in the skeleton thereof with one mole of a diisocyanate containing R9 in the skeleton thereof in a base oil.

Examples of the diisocyanate containing R9 in the skeleton thereof which can be suitably used include diphenylmethane diisocyanate, tolylene diisocyanate, xylylene diisocyanate, biphenylene diisocyanate, dimethyl-diphenylene diisocyanate, and alkyl substitution compounds thereof.

Examples of the monoamine containing a hydrocarbon group as R8 or R10 in the skeleton thereof which can be suitably used include aniline, cyclohexylamine, octylamine, toluidine, dodecylaniline, octadecylamine, hexylamine, heptylamine, nonylamine, ethylhexylamine, decylamine, undecylamine, dodecylamine, tetradecylamine, pentadecylamine, nonadecylamine, eicodecylamine, oleylamine, linolenoylamine, linolenylamine, methylcyclohexylamine, ethylcyclohexylamine, dimethylcyclohexylamine, diethylcyclohexylamine, butylcyclohexylamine, propylcyclohexylamine, amylocyclohexylamine, cyclooctylamine, benzylamine, benzhydrylamine, phenethylamine, methylbenzylamine, biphenylamine, phenylisopropylamine, and phenylhexylamine.

Also, examples of the monoamine containing a fused ring hydrocarbon group as R8 or R10 include indene based amine compounds such as aminoindene, amineindane, and amino-1-methyleneindene; naphthalene based amine compounds

such as aminonaphthalene (naphthylamine), aminomethyl-naphthalene, aminoethylnaphthalene, aminodimethyl-naphthalene, aminocadalene, aminovinylnaphthalene, aminophenylnaphthalene, aminobenzylnaphthalene, aminodinaphthylamine, aminobinaphthyl, amino-1,2-dihydronaphthalene, amino-1,4-dihydronaphthalene, aminotetrahydronaphthalene, and aminoctalin; fused dicyclic amine compounds such as aminopentalene, aminoazulene, and aminoheptalene; aminofluorene based amine compounds such as aminofluorene and amino-9-phenylfluorene; anthracene based amine compounds such as aminoanthracene, aminomethylanthracene, aminodimethyl-anthracene, aminophenylanthracene, and amino-9,10-dihydroanthracene; phenanthrene based amine compound such as aminophenanthrecene, amino-1,7-dimethylphenanthrecene, and amminoretene; fused tricyclic amine compounds such as aminobiphenylene, amino-s-indacene, amino-as-indacene, aminoacenaphthylene, aminoacenaphthene, and amino-phenalene; fused tetracyclic amine compounds such as aminonaphthacene, aminochrysene, aminopyrene, aminotri-phenylene, aminobenzanthracene, aminoaceanthrylene, aminoaceanthrene, aminoacephenanthrylene, aminoacephenanthrene, aminofluoranthene, and aminopleiadene; fused pentacyclic amine compounds such as aminopentacene, aminopentaphene, aminopicene, aminoperylene, aminodibenzanthracene, amino-benzopyrene, and aminocholanthrene; and fused polycyclic

(hexacyclic or polycyclic) amine compounds such as amino-coronene, aminopyranthrene, aminoviolanthrene, aminoisoviolanthrene, and aminoovalene.

The diurea compound represented by the foregoing formula (IV) may be used singly or in admixture and is blended in an amount of from 5 to 35 % by mass base on the whole amount of the grease composition. When the blending amount is less than 5 % by mass, it is difficult to keep the grease state, whereas when it exceeds 35 % by mass, the grease is excessively hardened so that the lubricating effect cannot be sufficiently revealed. Taking into consideration endurance under further high temperature, high speed, high load and high vibration conditions, in view of grease softening by high temperature and high shearing and lubricating effect, it is preferable that the blending amount is from 10 to 30 % by mass.

A worked penetration of the grease composition is preferably from 220 to 340. In order to make the worked penetration fall within this range by the blending amount of the diurea compound represented by the foregoing formula (IV), it is desired that a molar ratio of the alicyclic hydrocarbon group or aliphatic hydrocarbon group is 20 % by mole or more of the total sum of the aliphatic hydrocarbon group or aliphatic hydrocarbon group and the aromatic hydrocarbon group with the whole amount being defined as 100.

[Conductive powder]

For the purposes of eliminating a potential difference between the inner and outer races of bearing and preventing a flaking phenomenon from occurring, it is preferred to add a conductive powder. The conductive powder is not particularly limited. However, taking into consideration the matters that conductivity can be kept to a high temperature and that lubricity of the grease is not deteriorated, carbon based powders such as carbon black and carbon nano tube can be suitably used. The carbon black preferably has a mean particle size of not more than 5 μm , and more preferably not more than 2 μm . Most preferably, those having a mean particle size of from 10 to 300 nm are used. Such carbon black is available in the market, and examples thereof include KETJEN BLACK EC and KETJEN BLACK EC600JD, all of which are manufactured by Lion Akzo Co., Ltd. As the carbon nano tube, not only fullerenes of C60 and C70 but also those having a diameter of not more than 15 nm and a length of not more than 5 μm can be suitably used. Preferably, those having a diameter of not more than 10 nm and a length of not more than 2 μm are used. Such carbon nano tube is available in the market, and examples thereof include carbon nano fiber VGCF manufactured by Showa Denko K.K.

An addition amount of such a conductive powder in the grease composition is preferably from 0.5 to 5 % by mass

based on the whole amount of the grease composition. When the addition amount is not more than 0.5 % by mass, the addition effect is not obtained, whereas when it exceeds 5 % by mass, the fluidity of the grease is influenced. Also, when the foregoing mean particle size or length exceeds 2 μm , there is some possibility that the acoustic performance of the bearing is influenced.

[Rust preventive]

In the bearing for auxiliary machineries of automobile electrical components which is the application of the invention, high rust preventing properties are required, and therefore, it is preferred to add a rust preventive. Of rust preventives, rust preventives made of a carboxylic acid or a carboxylate, ester based rust preventives, and amine based rust preventives, all of which are low in a load against the environment, are preferable. In order to reveal sufficiently the rust preventing performance, these rust preventives are used in admixture of two or more kinds thereof, and the content thereof is from 0.2 to 10 % by mass in total and from 0.1 to 9.9 % by mass singly based on the whole amount of the grease composition. When the amount of the base oil is increased, the seizure resistance is improved. Accordingly, the amount of the rust preventives is preferably from 0.2 to 6 % by mass in total and from 0.1 to 5.9 % by mass singly.

Though the rust preventives made of a carboxylic acid or a carboxylate, the ester based rust preventives, and the amine based rust preventives are not particularly limited, preferred examples thereof are given below. Examples of the carboxylic acid or carboxylate include monocarboxylic acids such as stearic acid, dicarboxylic acids such as alkyl- or alkenylsuccinic acids and derivatives thereof, and metal (for example, calcium, barium, magnesium, aluminum, zinc, and lead) salts of naphthenic acid, abietic acid, a lanolin fatty acid, or an alkenylsuccinic acid. Of these, alkenylsuccinic acids and zinc naphthenate are suitable. Examples of the ester based rust preventives include sorbitan monooleate, sorbitan trioleate, pentaerythritol monooleate, and carboxylic acid partial esters of a polyhydric alcohol such as succinic half esters. Of these, sorbitan monooleate and succinic half esters are suitable. As the amine based rust preventives, alkoxyphenylamines, partial amides of a dibasic carboxylic acid, and the like are suitable.

[Other additives]

For the purpose of further enhancing the performance of the grease composition, other additives can be added as the need arises. Examples of other additives include antioxidants such as amine bases, phenol bases, sulfur bases, zinc dithiophosphate, and zinc dithiocarbamate;

extreme pressure agents such as phosphorus bases, zinc dithiophosphate, and organomolybdenum; oiliness agents such as fatty acids and animal and vegetable oils; and metal deactivators such as benzotriazoles. These can be added singly or in combinations of two or more kinds thereof. An addition amount of such additives is not particularly limited and properly set up so far as the prescribed object of the invention can be achieved.

(Rolling bearing)

Also, the invention relates to a rolling bearing having the foregoing grease composition packed therein. Though the rolling bearing is not limited with respect to the kind, construction and structure, for example, a double row angular ball bearing 10 illustrated in Fig. 1 can be enumerated. In the illustrated double row angular ball bearing 10, plural rolling elements (balls) 19, 19 are provided freely rollingly between double row outer raceways 17, 17 provided on the inner peripheral surface of an outer race 15 and inner raceways 18, 18 provided on the respective outer peripheral surfaces of inner races 16, 16, thereby making relative rotation between the outer race 15 and the inner races 16, 16 free. Also, an opening between the outer race 15 and the inner races 18, 18 is sealed by a sealing unit 1. This sealing unit 1 is one comprising a metallic slinger 2 having a sealing material 3 made of an elastic material integrally molded therewith.

The slinger 2 is constructed of a first member having an approximately L-shape cross-section and having an annular form as a whole, which is provided with an outer diameter side cylindrical portion 5 which can be freely internally fitted and fixed to the end part inner peripheral surface of the outer race 15 and an inside circular ring portion 6 which is folded internally in the diameter direction from the inner end edge in the axis direction of the outer diameter side cylindrical portion 5; and a second member having an L-shape cross-section and having an annular form as a whole, which is provided with an inner diameter side cylindrical portion 8 which can be freely externally fitted and fixed to the outer end part outer peripheral surface of the inner race 16 and an outside circular ring portion 9 which is folded externally in the diameter direction from the outer end edge in the axis direction of this inner diameter side cylindrical portion 8. The sealing material 3 is provided with three outer, intermediate and inner seal lips 3a, 3b, 3c; a tip edge of the outer seal lip 3a positioned in the outermost side is brought into slidable contact with the inner surface of an outer circular ring portion 9 constituting the slinger 2 along the entire periphery; and tip edges of the intermediate seal lip 3b and inner seal lip 3c, the both of which are the remaining two seal lips, are brought into slidable contact with the outer peripheral surface of the

inner diameter side cylindrical portion 8 constituting the slinger 2 along the entire periphery, thereby revealing a high sealing performance.

The foregoing grease composition is packed in a space formed by the outer race 15, the inner races 16, 16, the ball 19, and the sealing unit 1. Though a packing amount is not limited, it is preferable that the prelubricating amount accounts for from 25 to 45 % by volume of the foregoing space.

Since the foregoing grease composition is packed, the rolling bearing of the invention is well actuated even under severe conditions of high temperature, high speed, high load and vibration. Further, it does not generate abnormal noises even at an extremely low temperature of -40°C and therefore, is suitable for auxiliary machinery of automobile electrical component.

<EXAMPLES>

The invention will be further described below with reference to the following Examples and Comparative Examples, but it should be construed that the invention is not limited thereto in any way.

[Examples 1 to 8 and Comparative Examples 1 to 2]

(Preparation of test grease)

Each of test greases was prepared at a blending shown in Table 1. During this, a half amount of a base oil was

charged in a first vessel, into which was then thrown and dissolved cyclohexylamine. Furthermore, a half amount of a base oil was charged in a second vessel, into which was then thrown and dissolved diphenylmethane-4,4-diisocyanate. Then, the contents of the first vessel were added in the second vessel and reacted with stirring upon heating at about 70°C. Thereafter, the temperature was increased to 160°C, thereby stopping the reaction. After cooling, a rust preventive and an antioxidant were added, and the mixture was passed through a roll mill and deaerated, thereby obtaining a test grease. Incidentally, a blending amount of the rust preventive was 2 % by mass in total, and the kind and blending amount of the antioxidant were made common.

Using each of the thus prepared test greases, the following (1) seizure test-I, (2) low-temperature abnormal noise test-I, (3) high-temperature penetration change test and (4) rust preventing test were carried out. The results are also shown in Table 1.

(1) Seizure test-I:

1 g of the test grease was packed in a contact rubber seal-provided double row angular ball bearing having an inner diameter of $\phi 35$ mm, an outer diameter of $\phi 52$ mm, and a width of 20 mm (see Fig. 1), thereby preparing a test bearing. Then, the test bearing was subjected to continuous rotation under conditions at an outer race

rotation speed of $10,000 \text{ min}^{-1}$, a bearing temperature of 170°C and a radial load of 1,960 N, and when the bearing outer race temperature was increased by 15°C , it was considered that seizure occurred, and the test was stopped. The results were shown in terms of a relative value with the seizing life of Comparative Example 3 being defined as 1.

(2) Low-temperature abnormal noise test-I:

3.5 g of the test grease was packed in a contact rubber seal-provided single row deep groove ball bearing having an inner diameter of $\phi 25 \text{ mm}$, an outer diameter of $\phi 62 \text{ mm}$, and a width of 17 mm, thereby preparing a test bearing. Then, an operation of rotating the inner race at a rotation speed of $1,800 \text{ min}^{-1}$ for 5 seconds and then at $3,600 \text{ min}^{-1}$ for 5 seconds under conditions at -30°C and an axial load of 980 N was performed 5 times, thereby confirming the presence or absence of the generation of abnormal noises. The case where abnormal noises were generated was defined to be dissatisfactory.

(3) High-temperature penetration change test;

The test grease was coated in the state of a film having a thickness of 3 mm on an iron plate and then allowed to stand under the atmosphere at 170°C for 240 hours. After standing, a worked penetration was measured and compared with the worked penetration before standing. The case where a change of the worked penetration exceeded

± 100 was defined to be dissatisfactory.

(4) Rust preventing test:

2.7 g of the test grease was packed in a single row deep groove ball bearing having an inner diameter of $\phi 17$ mm, an outer diameter of $\phi 47$ mm, and a width of 14 mm, 0.3 mL of a 0.1 % sodium chloride aqueous solution was further poured into the bearing, and a non-contact seal was fitted, thereby preparing a test bearing. The test bearing was rotated so as spread the test grease and the sodium chloride aqueous solution all over the inside of the bearing and then allowed to stand under the environment at 60°C and 70 % RH for 3 days. After standing, the test bearing was broken up, and the inner raceway surface was observed, thereby confirming the presence or absence of the generation of rust. The case where rust was generated was defined to be dissatisfactory.

Table 1: Grease blending and test results

	Example 1 Diurea (aromatic + alicyclic)	Example 2 Diurea (alicyclic + aliphatic)	Example 3 Diurea (alicyclic)	Example 4 Diurea (aromatic + alicyclic)	Example 5 Diurea (alicyclic)
Amount of thickener % by mass	15	13	18	16	20
Construction of base oil	PE (100)	TE (100)	TE (100)	TE (100)	TE (100)
Hydrocarbon group of aromatic ester	C8 n-Octyl	C7 to C9 Mixed	C8 2-Ethylhexyl	C8', C10 n-Octyl, Decyl	C7 to C9 Mixed
Rust preventive	(Sorbitan trioleate) + (Alkenylsuccinic acid)	(Calcium naphthenate) + (succinic half ester)	(Zinc naphthenate) + (succinic half ester) + (sorbitan monooleate)	(Succinic half ester) + (Sorbitan monooleate)	(Sorbitan monooleate) + (zinc naphthenate)
Kinematic viscosity of base oil mm ² /s @40°C	83	53	90	48	70
Worked penetration	No. 2	No. 2 to No. 1	No. 1	No. 2	No. 3
Pour point of base oil °C	-38	-45	-40	-46	-48
High-temperature penetration change	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Low-temperature abnormal noise test-I	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Seizure test-I	11	10	14	7	12
Rust preventing test	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory

	Example 6	Example 7	Example 8	Comparative Example 1	Comparative Example 2
Thickener (alicyclic)	Diurea (aromatic + aliphatic)	Diurea (aliphatic)	Diurea (aromatic)	Triurea (aromatic)	Diurea (aromatic)
Amount of thickener % by mass	18	22	12	24	23
Construction of base oil	TE + ADE (30:70)	TE + PET (50:50)	TE (100)	TE (100)	MO (100)
Hydrocarbon group of aromatic ester	C7 to C9 Mixed	C10 Decyl	C12 Dodecyl	C8', C10 n-Octyl, Decyl	
Rust preventive	(Sorbitan monooleate) + (Zinc naphthenate)	(Stearic acid) + (Sorbitan monooleate)	(Zinc naphthenate) + (Alkenylsuccinic anhydride)	Succinic half ester	Sorbitan trioleate
Kinematic viscosity of base oil mm ² /s @40°C	80	60	130	48	97
Worked penetration	No. 1	No. 3 to No. 2	No. 2	No. 2	No. 2
Pour point of base oil °C	-40	-35	-25	-46	-25
High-temperature penetration change	Satisfactory	Satisfactory	Satisfactory	Dissatisfactory	Dissatisfactory
Low-temperature abnormal noise test-I	Satisfactory	Satisfactory	Dissatisfactory	Satisfactory	Dissatisfactory
Seizure test-I	9	7	10	4	1
Rust preventing test	Satisfactory	Satisfactory	Satisfactory	Dissatisfactory	Dissatisfactory

TE: Trimellitic ester

PE: Pyromellitic ester

PET: Pentaerythritol ester (30 mm²/s @40°C)

ADE: Dialkyl diphenyl ether (100 mm²/s @40°C)

MO: Mineral oil (97 mm²/s @40°C)

As shown in Table 1, the test greases of the Examples containing an aromatic ester oil-containing base oil and a diurea compound represented by the general formula (IV) as a thickener according to the invention are less in a change of the worked penetration at a high temperature and excellent in high-temperature endurance. Also, by packing each of the test greases of the Examples, the seizure life of bearing can be improved, the generation of abnormal noises at a low temperature can be suppressed, and further, the rust preventing properties are improved. However, as in Example 8, even by using an aromatic ester oil-containing base oil and using a diurea compound containing an aliphatic hydrocarbon group as a thickener, when the viscosity of the base oil is high, abnormal noises are generated at a low temperature. Also, as in Comparative Example 1, even by using an aromatic ester oil-containing base oil, when a triurea compound containing an aromatic hydrocarbon group is used as a thickener, the high-temperature endurance is deteriorated, and further, since the rust preventive is a succinic half ester singly, the

rust preventing performance is lowered.

(Verification-I of the content of aromatic ester oil)

Test greases were prepared according to the blending of the test grease of Example 7, except for using a base oil wherein the blending ratio of the trimellitic ester oil to the pentaerythritol ester oil was changed. Then, the foregoing (1) seizure test-I was carried out using these test greases.

The relationship between the content of the trimellitic ester oil and the seizure life is shown as a graph in Fig. 2. Incidentally, the seizure life is shown in terms of a relative value against the case of single use of the pentaerythritol ester oil (100%). As shown in the drawing, it is noted that when the trimellitic ester oil is contained in an amount of 30% by mass or more, the seizure life becomes especially good.

(Verification-I of the blending amount of thickener)

Test greases were prepared according to the blending of the test grease of Example 5, except for changing the blending amount of the thickener. Then, the foregoing (1) seizure test-I was carried out using these test greases.

The relationship between the blending amount of the thickener and the seizure life is shown as a graph in Fig. 3. Incidentally, the seizure life is shown in terms of a relative value against Comparative Example 3. As shown in the drawing, it is noted that when the thickener is

blended in an amount of from 5 to 35 % by mass, especially from 10 to 30 % by mass, the seizure life becomes good.

(Relationship-I between pour point of base oil and the generation of abnormal noises at a low temperature)

Base oils having a different pour point were prepared using a pentaerythritol ester having a pour point of -55°C and a pyromellitic ester having a pour point of -20°C, and a diurea compound containing an alicyclic hydrocarbon group was blended with each of the base oils, thereby preparing test greases. Incidentally, the blending amount of the diurea compound was made constant, and the worked penetration was adjusted at No. 2. Then, the foregoing (2) low-temperature abnormal noise test-I was carried out using these test greases.

The relationship between the pour point of the base oil and the generation of abnormal noises is shown in Fig. 4. It is noted that when the pour point of the base oil is not higher than -30°C, abnormal noises are not generated.

[Examples 9 to 15 and Comparative Examples 3 to 5]

(Preparation of test grease)

Each of test greases was prepared at a blending shown in Table 2. During this, a half amount of a base oil was charged in a first vessel, into which was then thrown and dissolved cyclohexylamine. Furthermore, a half amount of a base oil was charged in a second vessel, into which was

then thrown and dissolved diphenylmethane-4,4-diisocyanate. Then, the contents of the first vessel were added in the second vessel and reacted with stirring upon heating at about 70°C. Thereafter, the temperature was increased to 160°C, thereby stopping the reaction. After cooling, a rust preventive, an antioxidant and carbon black were added, and the mixture was passed through a roll mill and deaerated, thereby obtaining a test grease. Incidentally, the kind and blending amount of the antioxidant were made common.

Using each of the thus prepared test greases, the following (1) seizure test-II, (2) low-temperature abnormal noise test-I and (5) flaking resistance test were carried out. Also, the (3) high-temperature penetration change test and the (4) rust preventing test were carried out in the same manners as described above. The results are also shown in Table 2.

(1) Seizure test-II:

1 g of the test grease was packed in a contact rubber seal-provided double row angular ball bearing having an inner diameter of ϕ 35 mm, an outer diameter of ϕ 52 mm, and a width of 20 mm (see Fig. 1), thereby preparing a test bearing. Then, the test bearing was subjected to continuous rotation under conditions at an outer race rotation speed of $13,000 \text{ min}^{-1}$, a bearing temperature of 130°C and a radial load of 1,560 N, and when the bearing

outer race temperature was increased by 15°C, it was considered that seizure occurred, and the test was stopped. The case where the time for reaching the seizure was 1,000 hours or more was defined to be satisfactory.

(2) Low-temperature abnormal noise test-II:

3.5 g of the test grease was packed in a contact rubber seal-provided single row deep groove ball bearing having an inner diameter of $\phi 25$ mm, an outer diameter of $\phi 62$ mm, and a width of 17 mm, thereby preparing a test bearing. Then, the inner race was rotated at $2,600 \text{ min}^{-1}$ for 30 seconds under conditions at -30°C and an axial load of 9,800 N, thereby confirming the presence or absence of the generation of abnormal noises. The case where abnormal noises were generated was defined to be dissatisfaction.

(5) Flaking resistance test:

2.5 g of the test grease was packed in a single row deep groove ball bearing having an inner diameter of $\phi 17$ mm, an outer diameter of $\phi 47$ mm, and a width of 14 mm, thereby preparing a test bearing. This test bearing was integrated into an alternator of an actual engine, and the engine was repeatedly subjected to continuous rotation under the atmosphere at room temperature at from 1,000 to $6,000 \text{ min}^{-1}$ (the rotation number of bearing: 2,400 to $13,300 \text{ min}^{-1}$) under a pulley load of 1,560 N. At this time, a vibration value was measured, and when the vibration

value exceeded 5 times the initial value, it was considered that flaking occurred. The test was carried out 10 times, and the number of times of occurrence of the flaking was determined for a rotation time of less than 500 hours.

Table 2: Grease blending and test results

	Example 9	Example 10	Example 11	Example 12	Example 13
Thickener Amine Ratio	Diurea (aliphatic) 100	Diurea (alicyclic + aliphatic) 10/90	Diurea (alicyclic) 100	Diurea (alicyclic + aliphatic) 30/70	Diurea (alicyclic + aliphatic) 50/50
Amount of thickener % by mass	15	13	18	16	20
Construction of base oil	PE (100)	TE (100)	TE (100)	TE (100)	TE (100)
Hydrocarbon group of aromatic ester	C8 n-Octyl	C8 2-Ethylhexyl	C7 to C9 Mixed	C8, C10 n-Octyl, Decyl	C4 to C10 Mixed
Rust preventive addition amount	[sorbitan trioleate (2.5)] + [Alkenyl-succinic acid (2.5)]	[Calcium naphthenate (2)] + [Succinic half ester (2)]	[Zinc naphthenate (0.5)] + [Succinic half ester (2.5)] + [Sorbitan monooleate (2.5)]	[Succinic half ester (2)] + [Sorbitan monooleate (3)]	[Sorbitan monooleate (3)] + [Zinc naphthenate (1)]
Total:	5 %	Total: 4 %	Total: 5.5 %	Total: 5 %	Total: 4 %
Conductive substance	CB 1 %	CN + CB 0.5 % + 2 %	CB 5 %	CB 3 %	CN 3 %
Kinematic viscosity of base oil mm ² /s @40°C	83	90	53	48	100
Worked penetration	No. 2	No. 2 to No. 1	No. 1	No. 2	No. 3
Pour point of base oil °C	-38	-45	-48	-46	-48

	Example 9	Example 10	Example 11	Example 12	Example 13
High-temperature penetration change	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Low-temperature abnormal noise test-II	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Seizure test-II	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Rust preventing test	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Flaking resistance test	0/10	0/10	0/10	0/10	0/10

Table 2 (Cont'd.)

	Example 14	Example 15	Comparative Example 3	Comparative Example 4	Comparative Example 5
Thickener Amine Ratio	Diurea (alicyclic + aliphatic) 70/30	Diurea (aliphatic) 100	Diurea (aliphatic) 100	Triurea (aromatic) 100	Diurea (aromatic) 100
Amount of thickener % by mass	12	15	12	24	23
Construction of base oil	TE + ADE (30:70)	TE + PAO (50:50)	TE (100)	TE (100)	MO (100)
Hydrocarbon group of aromatic ester	C7 to C9 Mixed	C8 2-Ethylhexyl	C10 Decyl	C8, C10 n-Octyl, Decyl	
Rust preventive Addition amount	[Sorbitan monooleate (3)] + [Zinc naphthenate (4)]	[Succinic half ester 3] + [Sorbitan monooleate (3)] + [Zinc naphthenate (3.5)]	[Zinc naphthenate (0.5)] + [Alkenylsuccinic anhydride (0.5)]	Succinic half ester (0.5)	Sorbitan trioleate (0.5)
Total:	7 %	Total: 9.5 %	Total: 1 %	0.5 %	0.5 %
Conductive substance	CB + CN 4 %	CB 0.5 %	CB 7 %	-	-
Kinematic viscosity of base oil mm ² /s @40°C	80	60	160	48	97
Worked penetration	No. 1	No. 3 to No. 2	No. 4 to No. 3	No. 2	No. 2
Pour point of base oil °C	-40	-45	-15	-46	-25

	Example 14	Example 15	Comparative Example 3	Comparative Example 4	Comparative Example 5
High-temperature penetration change	Satisfactory	Satisfactory	Satisfactory	Dissatisfactory	Dissatisfactory
Low-temperature abnormal noise test-II	Satisfactory	Satisfactory	Dissatisfactory	Satisfactory	Dissatisfactory
Seizure test-II	Satisfactory	Satisfactory	Satisfactory	Satisfactory	Satisfactory
Rust Preventing test	Satisfactory	Satisfactory	Satisfactory	Dissatisfactory	Dissatisfactory
Flaking resistance test	0/10	0/10	0/10	3/10	4/10

TE: Trimellitic ester

PAO: Poly- α -olefin (48 mm²/s @40°C)

ADE: Dialkyl diphenyl ether (100 mm²/s @40°C)

MO: Mineral oil (97 mm²/s @40°C)

CB: Carbon black

CN: Carbon nano tube

As shown in Table 2, the test greases of the Examples containing an aromatic ester oil-containing base oil and a diurea compound represented by the general formula (IV) as a thickener according to the invention are less in a change of the worked penetration at a high temperature and excellent in high-temperature endurance. Also, by packing each of the test greases of the Examples, the seizure life of bearing can be improved, the generation of abnormal noises at a low temperature can be suppressed, and the rust preventing properties are improved. Further, by containing a conductive powder, the flaking resistance is improved. On the other hand, as in Comparative Example 3, in the test grease containing excessively a conductive powder, the acoustic characteristics are adversely affected, and abnormal noises are generated at a low temperature. Also, as in Comparative Example 4, even by using an aromatic ester oil-containing base oil, when a triurea compound containing an aromatic hydrocarbon group is used as a thickener, the high-temperature endurance is

deteriorated, and further, since the rust preventive is a succinic half ester singly, the rust preventing performance is lowered. Moreover, in Comparative Examples 4 and 5, since a conductive powder is not contained, the flaking resistance is also deteriorated.

(Verification-II of the content of aromatic ester oil)

Test greases were prepared according to the blending of the test grease of Example 15, except for using a base oil wherein the blending ratio of the trimellitic ester oil to the poly- α -olefin oil was changed. Then, the foregoing (1) seizure test-II was carried out using these test greases.

The relationship between the content of the trimellitic ester oil and the seizure life is shown as a graph in Fig. 5. Incidentally, the seizure life is shown in terms of a relative value against the case of single use of the poly- α -olefin oil (100%). As shown in the drawing, it is noted that when the trimellitic ester oil is contained in an amount of 30% by mass or more, the seizure life becomes especially good.

(Verification-II of the blending amount of thickener)

Test greases were prepared according to the blending of the test grease of Example 11, except for changing the blending amount of the thickener. Then, the foregoing (1) seizure test-II was carried out using these test greases.

The relationship between the blending amount of the

thickener and the seizure life is shown as a graph in Fig. 6. Incidentally, the seizure life is shown in terms of a relative value against Comparative Example 5. As shown in the drawing, it is noted that when the thickener is blended in an amount of from 5 to 35 % by mass, especially from 10 to 30 % by mass, the seizure life becomes good.
(Relationship-II between pour point of base oil and the generation of abnormal noises at a low temperature)

Base oils having a different pour point were prepared using a pentaerythritol ester having a pour point of -55°C and a pyromellitic ester having a pour point of -20°C, and a diurea compound containing an alicyclic hydrocarbon group was blended with each of the base oils, thereby preparing test greases. Incidentally, the blending amount of the diurea compound was made constant, and the worked penetration was adjusted at No. 2. Then, the foregoing (2) low-temperature abnormal noise test-II was carried out using each of the test greases.

The relationship between the pour point of the base oil and the generation of abnormal noises is shown in Fig. 7. It is noted that when the pour point of the base oil is not higher than -30°C, abnormal noises are not generated.

(Verification of the content of carbon black)

Test greases were prepared according to the blending of the test grease of Example 9, except for changing the

addition amount of carbon black. Then, the foregoing (5) flaking resistance test was carried out using these test greases, and a generation probability of flaking was calculated according to the following expression.

$$[\text{Generation probability of flaking (\%)}] = [(\text{Number of the generation of flaking}) / (\text{Number of tests}) (= 10)] \times 100$$

The relationship between the addition amount of carbon black and the generation probability of flaking is shown in Fig. 8. It is noted that by adding carbon black in an amount of 0.5 % by mass or more, the generation of flaking is suppressed.

(Verification of particle size of carbon black)

Test greases were prepared according to the blending of the test grease of Example 9, except for adding carbon black having a particle size of from 34 nm to 6 μm (however, the addition amount was made constant at 5 % by mass). Then, each of the test greases was packed in a single tow deep groove ball bearing having an inner diameter of $\phi 17$ mm, an outer diameter of $\phi 47$ mm, and a width of 14 mm such that the test grease accounted for 35 % of a spacial volume, thereby preparing a test bearing. The test bearing was subjected to rotation under the atmosphere at room temperature at an inner race rotation speed of $1,800 \text{ min}^{-1}$ under an axial load of 49 N, and an

anderon value (180 to 10,000 Hz) for 120 seconds after the start of rotation was measured. The case where the anderon value during this time is not more than 2.5 is considered to be satisfactory in the practical use.

The relationship between the particle size of carbon black and the anderon value is shown in Fig. 9. It is noted that by using carbon black having a particle size of not more than 5 μm , the flaking resistance can be imparted while keeping the acoustic characteristics.

<INDUSTRIAL APPLICABILITY>

According to the invention, there is provided a grease composition for auxiliary machinery of automobile electrical component, which does not generate abnormal noises even at an extremely low temperature of -40°C, has excellent seizure resistance even under a high temperature closed to 180°C, and has excellent flaking resistance and rust preventing performance. Also, according to the invention, there is provided a rolling bearing which is suitable for electrical parts, auxiliary machineries of engines, and the like.